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by

Christopher W. Allen

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Carbon chain polymers with pendant inorganic ring systems can be prepared by homo- or copolymerization reactions of cyclophosphazenes with olefinic exocyclic groups. The resulting polymers and copolymers exhibit flame retardancy and have a large number of reactive sites for further synthetic transformations. In alkenylpentafluorocyclotriphosphazenes the reactivity of the olefinic center may be mediated by placement of an electron donating group on the olefin or by the phosphazene. A broad range of homo- and copolymers have been prepared from vinyloxyphosphazenes. These materials undergo facile thermal decomposition. The volatile products of these processes have been identified and some insight has been gained into the kinetics and mechanism of the polymer thermolysis reactions.

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HYBRID INORGANIC-ORGANIC POLYMERS DERIVED FROM ORGANOFUNCTIONAL PHOSPHAZENES

by

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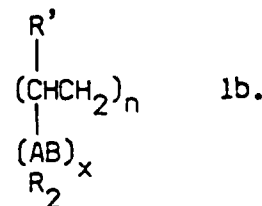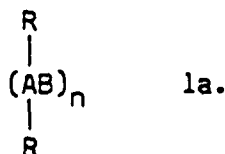Burlington, VT 05405

Carbon chain polymers with pendant inorganic ring systems can be prepared by homo- or copolymerization reactions of cyclophosphazenes with olefinic exocyclic groups. The resulting polymers and copolymers exhibit flame retardancy and have a large number of reactive sites for further synthetic transformations. In alkenylpentafluorocyclotriphosphazenes the reactivity of the olefinic center may be mediated by placement of an electron donating group on the olefin or by placing an insulating function between the olefin and the phosphazene. A broad range of homo- and copolymers have been prepared from vinyloxyphosphazenes. These materials undergo facile thermal decomposition. The volatile products of these processes have been identified and some insight has been gained into the kinetics and mechanism of the polymer thermolysis reactions.

INTRODUCTION

The primary approach to the development of main group inorganic polymer chemistry has been in the preparation, characterization and utilization of polymers with an inorganic backbone which may, or may not, be protected by organic substituents (1a). Important members of this class of materials which are discussed in this volume and elsewhere include:

$$\begin{array}{c} R \\ | \\ (AB)_n \\ | \\ R \end{array} \quad 1a. \qquad \begin{array}{c} R' \\ | \\ (CHCH_2)_n \\ | \\ (AB)_x \\ R_2 \end{array} \quad 1b.$$

$$R_2AB: R_2SiR_2Si; \ SS; \ R_2SiO; \ R_2PN; \ SN \qquad x = 2\text{-}4$$

poly(siloxanes), poly(phosphazenes) and more recently poly-
(silanes), poly(carbosilanes) and poly(silazanes). Our approach
has been to invert the roles of the organic and inorganic enti-
ties thereby producing polymers with carbon chain backbones and
inorganic substituents (1b). Vinyl polymers with transition
metal substituents have been studied extensively with most
interest being shown in metallocene derivatives.[1,2] Inorganic
main group entities as substituents on carbon chain polymers have
received sporatic study with the most interest being shown in
acyclic substituents involving organosilanes.[3] Vinyl carboranes
can also be polymerized and copolymerized to polymeric species
having the boron cluster as a substituent.[4] Our primary focus
has been on the use of organofunctional cyclophosphazenes as pre-
cursors to the desired polymers.[5] We have conducted a systematic
study of the effect of variation of both the phosphazene and ole-
finic components within the general structure of an organofunc-
tional phosphazene (2). These studies have allowed for both an
understanding of the polymerization behavior of this novel class
of monomers and the incorporation of certain of the useful pro-
perties, such as flame retardency, of the phosphazenes into tra-
ditional organic polymers.

$$X = Cl, F$$
$$R = Me, OEt, OMe$$
$$Y = N, NPX_2N$$
$$E = O, C_6H_4$$
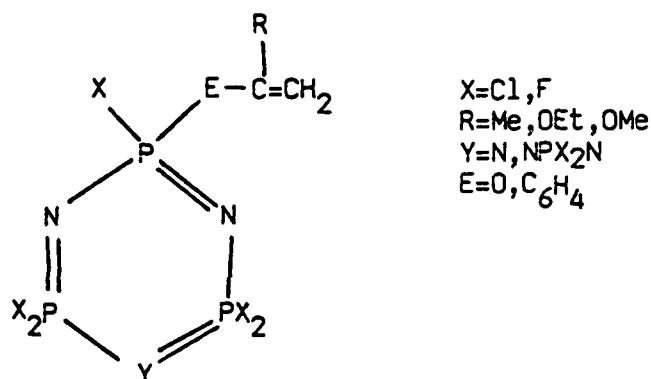
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ALKENYL PHOSPHAZENES

We intially demonstrated that our basic approach was feasible
by preparing copolymers (3; R=Me) of 2-(propenyl)pentafluoro-
cyclotriphosphazene (4) and styrene or related monomers.[6,7]
The copolymers, which have good solubility and thermal stability,
do not burn or produce smoke when exposed to a flame. Nucleo-
philic substitution reactions of the types which are well known
in phosphazene chemistry[8] can be carried out on the phosphazene
moiety in these copolymers thus allowing for the preparation of a
broad spectrum of related materials.[7] However, the strong
electron withdrawing nature of the $N_3P_3F_5$ unit[9] transforms the
propenyl group into a highly polar olefin which undergoes com-
petitive anionic addition in the course of its preparation[13] and
serves as a termination site in the copolymerization reaction.[6]

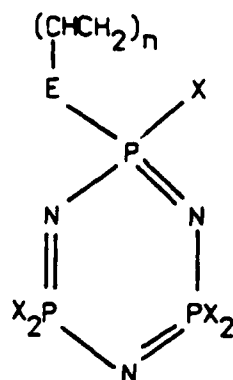$$[(CRCH_2)_x(\overset{\underset{\displaystyle Ph}{|}}{C}HCH_2)_y]_n$$
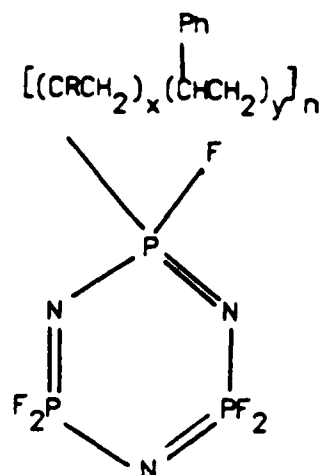
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The electron deficient nature of the olefin can be mediated in two ways either by placement of an electron donating substituent on the olefin[11] or by insulating the olefin from the phosphazene ring by other groups. The introduction of an alkoxy function as the electron donating group on the olefin leads to 2-(1-ethoxy vinyl)pentafluorocyclotriphosphazene, $N_3P_3F_5C(OEt)=CH_2$ (5).[11] A comparison of the ^{13}C nmr chemical shifts of the olefinic β-carbon in 4 and 5 gives evidence for a significant reduction in the olefin polarity by addition of the electron donating ethoxy function. The change in olefin polarity is also demonstrasted by the absence of anionic addition to the olefinic center in 5. Facile copolymerization of 5 with styrene or methylmethacrylate occurs to yield materials (e.g. 3; R=OEt) with higher degrees of phosphazene incorporation but properties similar to the copoly-mers derived from 4. The use of an aryl group as an insulating function[13,14] is exemplified in α-methylstyrylphosphazenes such as the meta and para isomers of $N_3P_3F_5C_6H_4C(CH_3)=CH_2$ (6) which also have been induced to undergo copolymerization with styrene and methylmethacrylate.[14] These later compounds have the highest degree of phosphazene incorporation into copolymers which we have yet observed. Reactivity ratio and Q,e calculations show that, in general, (i.e., in 4,5,6) the phosphazene moiety exhibits a very strong electron withdrawing effect without any significant mesomeric interaction. Thus, the model of the electronic struc-ture of the olefinic center in alkenylphosphazenes which arises from quantitative studies of reactivity in copolymerization reac-tions is very similar to that deduced from spectroscopic studies of arylphosphazenes.[9]

Further examination of these reactivity and Q,e data allow for a clear understanding of the polymerization behavior and how it is modified by the phosphazene. Although most systems are best described by the terminal model, the reactivity patterns exhibited in the copolymerization of α-methylstyryl penta-fluorocyclophosphazene (6) with methylmethacrylate can only by quantitatively fit by a pennultimate model.[14]

In order to obtain homopolymers from the organofunctional phosphazenes, monosubstituted rather than 1,1-disubstituted olefins of the type described above, are required. The styrene derivative, $N_3P_3F_5C_6H_4CH=CH_2$, was prepared from the phenylmethyl ether derivative, $N_3P_3C_6H_4C(OMe)=CH_2$, via hydrostannation and subsequent β-elimination of the trialkyltin methoxide.[14] Polymerization of the styryl phosphazene lead to a high molecular weight polymer with pentafluorocyclotriphosphazene units at the para position of each phenyl group (7; $E=C_6H_4$, $X=F$). The TGA of this material shows a significant retention of involatile material to over 1000°, suggesting the intriguing possibility

$$(\overset{\underset{|}{E}}{C}HCH_2)_n$$

```
        (CHCH2)n
         |
      E       X
       \     /
         P
       //  \
      N     N
      ||    |
    X2P    PX2
       \   /
         N
```

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of using the pyrolysis of polymers of type 1b as a new route to ceramic solids.

VINYLOXYPHOSPHAZENES

In an attempt to generate convenient routes to organofunctional phosphazenes which could undergo homopolymerization reactions, we explored the reactions of lithium enolates, particularly that of acetaldehyde, with halophosphazenes which leads to the series of organofunctional monomers $N_3P_3Cl_{6-n}(OCH=CH_2)_n$[15,16] (n=1-6), $N_3P_3F_{6-n}(OCH=CH_2)_n$ (n=1-5)[17] and $N_4P_4Cl_{8-n}(OCH=CH_2)_n$ (n=1,2).[18] In these systems, an oxygen atom acts as the insulating function between the phosphazene and the olefin. Other, related monomers, can be prepared by nucleophilic substitution reactions with, for example alkoxide ions, of the chlorine atoms in $N_3P_3Cl_5OCH=CH_2$ (8). The appropriate monosubstituted derivative (n=1) in many cases has been polymerized by radical initiation to yield the linear high polymer with a cyclophosphazene moiety as part of each repeating unit, e.g. 7; $E=O$, $X=Cl$.[19] However, not all of the vinyloxyphosphazene monomers will undergo radical polymerization; those with amino substituents are unreactive. The ^{13}C nmr data indicate that these species electronically resemble vinyl ethers (which do not undergo radical polymerization) whereas the reactive derivatives resemble vinyl acetate. These data demonstrate an excellent example of electronic effect transmission in cyclophosphazene systems.

The large number of reactive sites per monomer unit in these highly functionalized polymers has allowed for further synthetic

transformations based on the chemistry of the phosphazene unit thereby allowing preparation of the amino substituted polymers by reaction of 7 (E=O, X=Cl) with the appropriate amine. The broad range of vinyloxyphosphazene monomers which are available allow for the formation of copolymers of two different organofunctional phosphazene monomers. Consequently, we can apply polymerization reactivity studies to directly explore differences in chemical behavior based on changes in substituent, ring size, etc. of the inorganic monomer. We have prepared a series of copolymers of 8 and its tetrameric analog, $N_4P_4Cl_7OCH=CH_2$ and shown that 8 has the greater reactivity in this system. In a joint study with Dr. van de Grampel of the University of Groningen, we have explored the copolymerization of 8 with a vinyloxycyclophospha-(thia)zene.[20]

As opposed to the alkenylphosphazene polymers, the vinyloxychlorophosphazene polymers are thermally labile undergoing an exothermic decomposition via HCl elimination as low as 100° followed by a more complex endothermic process at higher temperatures. The first step represents a mild thermal cross-linking reaction with low weight loss. The solid state kinetics of this first step have been measured. The activation energy for the first step is greater for the tetramer than for the trimer derivative. Since this is the reverse of the behavior observed for displacement reactions of the $(NPCl_2)_3$ and $(NPCl_2)_4$[8], it implies that the barrier is primarily associated with the chain reorganization energy needed to bring the phosphorus-chlorine bond in proximity with a carbon-hydrogen group. After the exothermic cross-linking step, there is a second process which appears to result in the elimination of oxobridged phosphazene dimers, e.g. $(N_3P_3Cl_5)_2O$ and, by implication, to build an oxo cross-link between the polymer chains. Copolymerization with organic monomers suggest a similarity of behavior between the vinyloxyphosphazene and vinylacetate. The thermal lability of the polymers containing the vinyloxyphosphazene is even more pronounced in the copolymers. In order to overcome some of these problems a larger insulating function was sought. The reactions of 2-hydroxyethyl methylmethacrylate with $N_3P_3Cl_6$ leads to $N_3P_3Cl_5OCH_2CH_2OC(O)C(CH_3)=CH_2$ which undergoes radical or thermal homo and copolymerization which if not carefully controlled is accompanied by extensive cross-linking.

EXTENSIONS TO OTHER SYSTEMS

Our studies have convinced us that this approach to hybrid organic-inorganic polymers is a valuable one leading to a wide variety of new, interesting, materials. In addition to new phosphazenes, we are now expanding our studies to the preparation of pentamethylvinylcyclotriborazene polymers and we are investigating various silicon containing systems.

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